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⑭ 発明の名称 蛍光体組成物

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明 細 書

1. 発明の名称

蛍光体組成物

2. 特許請求の範囲

1. 一般式 $Zn_{1-a}Mg_aS:Pr^{3+}$, $0 < a \leq$ 0.20 で表わされ、母体組成が硫化亜鉛と硫化マグネシウムの固溶系から成り、主発光が Pr^{3+} によりもたらされることを特徴とする蛍光体組成物。2. $0.05 \leq a \leq 0.10$ で表わされることを特徴とする特許請求の範囲第1項記載の蛍光体組成物。

3. EL素子を構成する発光層の少なくとも一成分が、特許請求の範囲第1項記載の蛍光体組成物から成ることを特徴とするEL素子。

4. 製造して特許請求の範囲第1項記載の蛍光体組成物が得られることを特徴とする蒸発源ターゲット。

3. 発明の詳細な説明

(産業上の利用分野)

本発明は、主発光が青緑色から深赤色領域にある新規蛍光体組成物 (Zn, Mg) $S:Pr^{3+}$ に係わり、白色EL表示および照明用光源に適用して優れた特性を示す蛍光体の組成に関する。

(従来の技術)

(Zn, Mg) S 母体および当該母体に発光イオンを導入した従来例に下記の文献がある。

1) ジャーナル・オブ・エレクトロケミカル・サイアティ 99巻, 4号, 155頁から158頁 [J. Electrochemical Soc. 99 (4) 155~158 (1952)]

本文献においては、 MgS 25モル%以下、残りは ZnS から成る (Zn, Mg) S 母体に Cu, Ag, Pb, As, Sb, Bi および、 $Cu-Mn, Pb-Mn, Cu-Pb$ をそれぞれ付活した蛍光体について、紫外線励起ならびに電子線励起による発光特性が示されている。

2) ジャーナル・オブ・マテリアルサイエンス 21巻, 2100頁から2108頁 [J. of Material Science 21 2100~2108]

(1985)]

本文献においては、 $Zn_{1-x}Mg_xS:Cu, Br$ を用いた分散型ELの発光ピーク波長は、 x の増大に伴い、525nmから436nmまでシフトすると報告されている。

- 3) ラシアン・ジャーナル・オブ・インオーガニック・ケミストリー 9巻, 4報, 512頁から516頁 [Russian J. of Inorganic Chemistry 9 (4) 512~516 (1964)]

本文献においては、 MgS は ZnS に対して22モル%まで固溶し、かつ固溶量の増大に伴い六方晶系の格子定数 a_0, c_0 はともに増大すると記載されている。

次に、 MgS を固溶しない ZnS 母体に Pr^{3+} を付活した蛍光体については下記の文献がある。

- 4) エス・アイ・デー 80ダイジェスト106頁~107頁 [SID 80 Digest, p106~107, (1980)]

本文献には、発光層 $ZnS:PrF_3$ を Si_3N_4 絶縁層と Y_2O_3 絶縁層で挟んだ薄膜

光しても極めて輝度が低い。

次に、従来例3)は発光イオンを導入しない母体のみに係わり、外部からのエネルギー付与により充分な発光(自己付活発光)は得難い。また、従来例4), 5)は ZnS 母体に本発明と同じ Pr^{3+} を導入した蛍光体であるが、白色表示を得るには520~620nm領域の発光が弱いのが欠点である。

さらにまた、従来例6)は、白色表示を得るには素子構成が複雑になると言う欠点がある。

本発明の目的は、上述の問題点の多くを解決した新規の蛍光体組成物を提供することにある。

〔課題を解決するための手段〕

上記目的は、EL遷移が青緑色から深赤色に分布する Pr^{3+} を発光イオンに選定し、かつ Pr^{3+} の導入を容易ならしめるように ZnS 系母体格子の拡大をはかることにより達成される。

周知のように、 Pr^{3+} のイオン半径 $r=1.09\text{\AA}$ に対して Zn^{2+} のそれは $r=0.74\text{\AA}$ と小さいため、所要量の Pr^{3+} を導入するには母体格子の

EL素子の電圧-輝度特性が示されている。

- 5) フিজカ・ステイタス・ソリディ a69巻の11頁-66頁 [Physica Status Solidi a69 11~66 (1982)] の36頁

本文献には $ZnS:PrF_3$ のEL発光スペクトルが他の希土類弗化物付活の場合と比較して示されている。

一方、EL素子の構成に関しては、例えば

- 6) 特開昭61-49387 には、赤色、緑色、青色のいずれか一色の発光EL素子を一枚の透明基板に形成し、残り二色の発光EL素子を別個の一枚の透明基板に形成し、両基板を対向して配置したことを特徴とするフルカラー薄膜EL素子が開示されている。

〔発明が解決しようとする課題〕

上記の従来例のうち、1), 2)は Pr^{3+} とは異なる発光イオンを導入した蛍光体に係わり、いずれも600nmより長波長域の赤色発光成分に欠ける。また、これらの蛍光体を出発原料に用いて作成した薄膜EL素子は全く発光しないか、発

拡大が望まれる。母体格子拡大の一手段として ZnS に MgS を固溶させる。例えば、 ZnS に22モル%の MgS を固溶させると六方晶系となり、格子定数 a_0 は1.9%, 格子定数 c_0 は1.1%増大する。

また、 Zn^{2+}, Mg^{2+} のような二価陽イオン格子点に Pr^{3+} のような三価の発光イオンを導入するに際して、 Mg 原料には、 MgO から出発した中間原料に代つて、高純度の Mg 金属から出発した中間原料を使用し、硫酸根や酸素イオンの介入を極力抑制する焼成方法を採用した。

〔作用〕

本発明の第1の利点は、 ZnS から $(Zn, Mg)S$ へ母体格子を拡大することにより輝度最適化のための Pr^{3+} 濃度の調整がより容易になる点であり、 Pr^{3+} に限らず他の三価希土類イオンの ZnS への導入に際して、充分な濃度の導入困難の常識を打破する汎用性のある手段をも開示している。例えば薄膜EL素子においては、発光層内 Pr^{3+} 濃度の上限を ZnS 母体の場合と比較し

て一桁以上高めることが出来る。

第2の利点は、従来の蛍光体 $ZnS:Pr^{3+}$ では弱い520~620nm領域の発光がMgS固溶体によつて増大し、かつMgS固溶量に依存して発光強度の調整が可能になる点である。さらに、薄膜EL素子においては、駆動周波数によつても発光強度の調整が可能になる。この結果、上記第2の利点を生かして相関色温度2300Kから5000Kまで、即ち温白色から昼白色までの適用分野に応じた幅広い白色表示または白色照明を得ることが出来る。

〔実施例〕

以下、実施例に従つて本発明を説明する。

実施例1

一般式 $Zn_{1-a}Mg_aS:Pr$ において、 $a > 0$ が本発明の特徴である。 $a > 0$ の効果がMg原料中の不純物、特にMgと共に混入容易な酸素不純物によるものでないことを明確にするため、二種類のMg原料を用いて、第1図の流れ図に従つて蛍光体合成、蒸着用のターゲットを作成し、さら

に当該ターゲットから薄膜EL素子を作成した。

二種類のMg原料は共にMgSO₄で表わされ99.9%以上の純度を有するが、その出発原料が異なる。今、MgOから出発したものを(A)、高純度Mg金属から出発したものを(B)と略記する。まず、(A)、(B)を用いて $a = 0.1$ 即ち $Zn_{0.9}Mg_{0.1}S:0.03Pr$ の組成をもつターゲットを第1図に従つて作成し分析した結果、(B)法では(A)法と比較して、Caは700ppmから20ppmに、Cr, Mn, Fe, Cuは220ppmから10ppm以下に低減することを確認した。これら不純物濃度に相応して酸素不純物濃度も低減しているものと推定される。

次に、上記(A)、(B)のターゲットを蒸着源に用いて、EB(電子線)蒸着法による通常の三層構造薄膜EL素子を作成した。発光層を挟む絶縁膜には、よく知られたY₂O₃を使用した。得られた素子の特性比較例を第1表に示す。表から明らかなように、同一層厚の発光層を有する素子

について、(B)法原料から出発すると、発光開始電圧、相対輝度、周波数特性のいずれもが(A)法と比較して良好となることがわかった。

第1表

Mg原料の種類	発光層の膜厚(μm)	発光開始電圧V _{th} (V)	(V _{th} +30)Vにおける相対輝度L(%)	周波数特性のべき数、 $n[L \propto f^n]$
A	0.66	188	100	0.71
B	0.66	162	148	0.95

以上、本発明の特徴であるMg含有蛍光体では、まずもつてMg原料純度の諸特性に及ぼす効果が著しいこと、換言すれば、純化したMg原料を用いてはじめてその効果が具現出来るものであることが本実施例によつて明らかとなった。

実施例2

一般式 $Zn_{1-a}Mg_aS:Pr^{3+}$ において、 Pr^{3+} 濃度を0.03モル一定としてMgS固溶量を表わすa値を $a = 0$ (比較例)、0.01、0.05、0.10、0.15の5段階に変化した

組成をもつ蒸着源ターゲットを実施例1と同じ手法で作成した。ここでMg原料には実施例1で諸特性が良好と確認された(B)法を用いた。

上記ターゲットからEB蒸着法により通常の三層構造薄膜EL素子を作成した。発光層の膜厚は第1表の場合と同様に0.66μm一定とした。

周波数5KHz、正弦波駆動下における相対輝度、色度座標、ならびに色度座標から算出した相関色温度をまとめて第2表に示した。表の相対輝度は、 $a = 0$ 即ちMgSを固溶しない公知蛍光体 $ZnS:0.03Pr$ の発光開始電圧V_{th}プラス30Vにおける輝度を基準として、 $a > 0$ の素子についても同様にプラス30Vにおいて実測した値の相対値である。

表から明らかなように、 $a > 0$ では $a = 0$ の素子より高い輝度が得られ、 $a = 0.05$ において最高値173%が得られた。なお、 $a > 0.15$ についても蛍光体合成ならびに素子化を試みたが、輝度特性のばらつきが大きくなり、平均輝度は100%前後にとどまった。先に引用した公知例

の1)および3)から推察した $a = 0.22 \sim 0.25$ 、即ちZnSに対するMgSの固溶限22~25モル%に近いための現象と考えられる。

第2表

a	相対輝度 (%)	色 度 座 標		相関色温度 (K)
		x	y	
0 (比較例)	100	0.354	0.434	5000
0.01	104	0.387	0.426	4200
0.05	173	0.451	0.357	2400
0.10	143	0.469	0.372	2300
0.15	110	0.452	0.394	2700

次に第2表の色度座標に着目すると、 a 値の増加に対して色度座標の y 値は必ずしも単調と言うわけではないが、むしろ減少の傾向にあり、上述の a 値の増加に伴う輝度向上が見掛け上の y 値の増加によるものではないことを示す。なお、色度座標は駆動周波数によっても変化することが見出された。例えば、5 KHzと1 KHzにおける

組成をもつ発光層を約1 μ m蒸着した二層構造の試料を対象にして、 O_2^+ イオン照射により二層構造膜の0.8 mm^2 領域の膜厚方向Mg/Zn, Pr/Zn, Y/Znの分布を調べた結果である。図から、膜厚方向の発光イオン Pr^{3+} の分布は母体のMgの分布とよく対応していることがわかる。 Pr^{3+} がMgの存在下で有効に導入されることを裏付けている。

実施例3

電界以外の励起によるMgSあり、なしの輝度比較を目的として、まず下記組成物の合成を行なった。比較に供した試料は、実施例1, 2の場合より Pr^{3+} 濃度を一桁低くし、母体組成は一般式において $a = 0.05$ に相当する $Zn_{0.95}Mg_{0.05}S$ ならびに $a = 0$ に相当するZnSとした。第1図の流れ図に従って上記の組成物を秤量、乾式混合(図中の符号2)した後、当該混合物の100gを透明石英ボートに自重で充填し、図の符号3の工程を省略してAr流量200 ml/min , 1000で、2時間焼成した。焼成の前後には一昼夜Ar

色度差 $|\Delta x|$, $|\Delta y|$ は、 $a = 0$ のZnS: Pr^{3+} では最大0.001であるのに対して、 $a = 0.05$ では最大0.021と1桁以上大きくなることがわかった。

第2図は、最高輝度が得られた $a = 0.05$ 、即ち $Zn_{0.95}Mg_{0.05}S : 0.03 Pr$ からなる素子の5 KHz、正弦波駆動下の発光スペクトルである。これを先に引用した公知例5)に記載のZnS: Pr^{3+} の発光スペクトルと比較すると、520~620 nm領域の発光強度が増大しており、MgSを5モル%導入するだけで Pr^{3+} のJ状態の混合が起り発光遷移確率が増大したものと考えられる。 $a > 0$ では、上記波長域の発光強度増大の他に、周波数によらず青緑色発光よりも深赤色発光が強く現われる傾向にあり、この結果、第2表に記載したような a に依存した大幅な相関色温度の変化が得られた。

第3図は、通常の三層構造薄膜EL素子作成プロセスに従って、あらかじめガラス基板上に Y_2O_3 絶縁膜を蒸着し、その上に $a = 0.05$ の

ガスを放流した。

次に、得られた粉末蛍光体を水沈降塗布して、電子線励起による粉末輝度を比較した。励起の条件は、加速電圧27 KV、電流密度0.16 $\mu A/cm^2$ である。 $a = 0$ に相当する公知蛍光体ZnS: $0.003 Pr^{3+}$ の輝度を基準にして、本発明に係わる $a = 0.05$ 相当 $Zn_{0.95}Mg_{0.05}S : 0.003 Pr^{3+}$ では3.6倍の輝度が得られた。
【発明の効果】

以上説明したように、本発明では公知蛍光体ZnS: Pr^{3+} の母体にMgSを固溶させることにより、母体格子を拡大させて、発光イオン Pr^{3+} の導入を容易にし、薄膜EL素子の発光層に適用して同一製膜法のZnS: Pr^{3+} 含有EL素子と比較して1.7倍の輝度が得られる。また、MgS固溶量の調整により5000 Kから2300 Kの大幅な相関色温度調整が可能となる。MgS固溶の効果は上記の薄膜EL素子に限定されるものではない。電界以外のエネルギー付与によつても、過去、現在を問わずZnSの適用実績のある分野

であれば、 Pr^{3+} 濃度と MgS 固溶量の最適化により効果を達成し、電子線励起の輝度は従来蛍光体の3倍を超える。

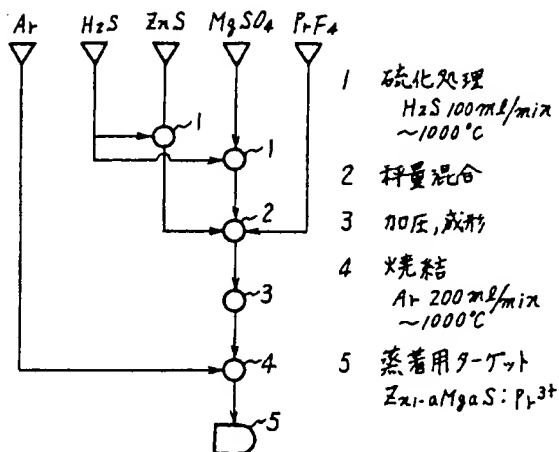
Pr^{3+} は、本来、可視の幅広い波長域の発光をもたらすため、視認性を重視する白色表示素子や白色照明用光源に適用して効果があり、特に暖色系の白色が要求される分野ではその効果が著しい。

なお、本発明は Mg 含有母体に Pr^{3+} を導入して効果を奏するものであるが、 Pr^{3+} 以外の発光イオンが微量導入されていても Pr^{3+} 発光の効果が損われるものではない。

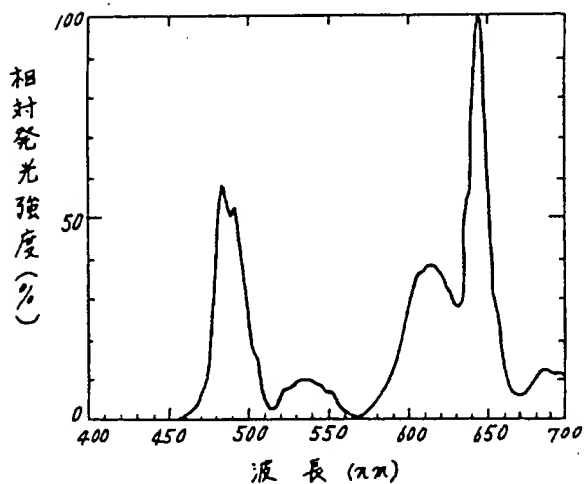
4. 図面の簡単な説明

第1図は本発明の実施例に記載した蛍光体組成物の合成方法ならびにそれを用いた蒸発源ターゲットの作成方法を示す流れ図、第2図は $\text{Zn}_{0.98}\text{Mg}_{0.02}\text{S} : 0.03\text{Pr}$ を発光層とする薄膜EL素子の発光スペクトル図、第3図は第2図発光層内膜厚方向構成イオン分布を示す図である。

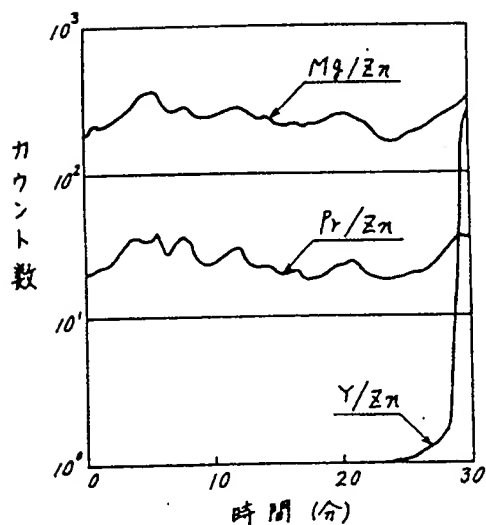
第1図



第2図



第3図



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Details

1. Name of invention
Phosphor composition material

2. Range of the patent claim

- 1) It is a phosphor composition material which shall be characterized by being indicated by the ordinary formula of $\text{Zn}_{1-a}\text{Mg}_a\text{S} : \text{Pr}^{3+}$, $0 < a \leq 0.20$, which the main composition is composed of solid solution of zinc sulfide and magnesium sulfide, and having the main emitting from Pr^{3+} .
- 2) It is concerning the phosphor composition material, which is stated in the aforementioned (1) of the range of the patent claim, which shall be characterized by being indicated by $0.05 \leq a \leq 0.10$.
- 3) It is an EL element, which shall be characterized by making at least one component of the emission layer, which composes the EL element, shall be made of the phosphor composition material which is mentioned in (1) of the range of the patent claim.
- 4) It is a vapor source target which shall be characterized by obtaining the phosphor composition material, which is mentioned in the (1) of the range of the patent claim, by forming.

3. Detailed explanation of the invention

[Utility field of the industry]

This invention is concerning the composition of the phosphor, which shall indicate the excellent characteristics and is suitable for the use of white color EL display and light source for illumination, and shall be related to the $(\text{Zn}, \text{Mg})\text{S} : \text{Pr}^{3+}$, which is the new phosphor composition material, which shall have the main emitting within the area between the blue green color and deep red color.

[Existing technique]

Existing examples which introduced the emitting ion to the $(\text{Zn}, \text{Mg})\text{S}$ bus (bus-bar) and the said host material are written in the documentary records, which are mentioned below.

- 1) The emitting characteristics of the ultraviolet light excitation and the electron beam excitation concerning the phosphor material, which Cu, Ag, Pb, As, Sb, Bi, Cu – Mn, Pb – Mn and Cu – Pb are added to the host material of $(\text{Zn}, \text{Mg})\text{S}$, which is composed of MgS less than 25 mol% and ZnS , were written on page 155 to page 158, Vol. 99 (4) of the Journal of Electrochemical Society (1952).
- 2) It is reported that the emission peak wavelength of the scattered EL, which shall use $\text{Zn}_{1-x}\text{Mg}_x\text{S} : \text{Cu}, \text{Br}$, shall be shifted from 525 nm to 436 nm together with the increase of x, on page 2100 to page 2108, Vol. 21 of the Journal of Material Science (1985).

- 3) Page 512 to page 516, Vol. 9 (4) of the Russian Journal of Inorganic Chemistry mentioned that the MgS shall solidly dissolve up to 22 mol% against the ZnS, and when the amount of the solid solution increases, both a_0 and c_0 of the hexagonal lattice constant shall also increase.

Next, the phosphor, which Pr^{3+} is added to the ZnS host material, which shall not make solid solution of MgS, is written in the documentation records, which are mentioned below.

- 4) In the S I D 80 Digest, Page 106 to Page 107 (1980), Voltage and luminance characteristics of the thin film EL element, which the emission layer of ZnS : PrF_3 shall be sandwiched between the insulation layer of Si_3N_4 and another insulation layer of Y_2O_3 is shown.
- 5) In the 36 pages within the Physics Status Solidi, a69, Page 11 to Page 66 (1982) shall indicate the comparison between the EL emitting spectrum of ZnS : PrF_3 and the case when other rare earth compounds are added.

On the other hand, concerning the structure of EL element, the example is as follows.

- 6) In the TOKUKAISHO 61-49397, it indicates such full-color thin film EL element which features that it consists of 2 substrates which are the transparent substrates that one of the emitting EL elements of red, green or blue, is formed on, and another transparent substrate which the emitting EL element of the remaining two colors are formed on and that both substrates are arranged at the facing way to each other.

[Problems to be solved by the invention]

Above (1) and (2) within the abovementioned existing examples are concerning the phosphor, which introduced the emitting ion, which is different from Pr^{3+} , and both of them shall not have a sufficient amount of red color emitting component of the longer wavelength than 600 nm. Also, the thin film EL element, which is created using these phosphor materials as the initial (starting) raw material shall not emit at all or even if it does, the luminance would be extremely low.

Next, the above (3) of the existing example is only related to the host material which shall not introduce the emitting ion, and it is very difficult to obtain the sufficient emitting (self emitting) by adding the energy from outside. Also, concerning the above (4) and (5) of the existing examples, although they are the phosphor material which introduced the Pr^{3+} , which is the same material as the one used in the invention, to the ZnS host material, there is a disadvantage that the emitting of the area of 520 nm to 620 nm, which is necessary to have in order to obtain the white color display, is weak.

Further, the above (6) of the existing example shall have a weak point in the structure of the element, which shall become complicated in order to obtain the white color display.

The purpose of this invention is to provide the new phosphor composition material, which has solved many of the abovementioned problems.

[Method of how to solve the problem]

The abovementioned purpose shall be accomplished by selecting Pr^{3+} as the emitting ion, which the E1 transition shall distribute from the blue green color to the deep red color as well as enlarging the ZnS host material lattice in order to introduce Pr^{3+} easily.

As it is known, the ion radius of Zn^{2+} is $r = 0.74 \text{ \AA}$, which is small compared to the ion radius of Pr^{3+} , which is $r = 1.09 \text{ \AA}$, therefore, in order to introduce designated amount of Pr^{3+} , the expansion of the host material lattice shall be desired. One of the methods to expand the host material lattice is to make MgS into solid solution to ZnS. For example, when MgS of 22 mol% is made into solid solution to ZnS, it shall become hexagonal crystal, and the lattice constant a_0 shall be increased by 1.9%, and the lattice constant c_0 shall be increased by 1.1%.

Also, when introducing the emitting ion of the 3 atoms of Pr^{3+} , etc. to the lattice point of the positive ion of the 2 atoms such as Zn^{2+} or Mg^{2+} , etc., intermediate raw material which shall begin with high purity Mg metal shall be used instead of the intermediate raw material which shall begin with MgO, for the use of Mg raw material, and such firing method to control from intervening of silver sulfide and oxygen ion to the utmost is adopted.

[Function]

The first advantage of this invention is that the adjustment of Pr^{3+} density in order to make the best luminance becomes easier by enlarging the host material lattice from ZnS to (Zn, Mg) S, and the universal method to obtain sufficient density in connection with the introduction of other rare earth ion of 3 atoms than Pr^{3+} to ZnS, which is breaking the common sense concerning introducing sufficient amount of density, which is supposed to be very difficult until now, is also mentioned. For example, concerning the thin film EL element, the upper limit of the Pr^{3+} density within the emission layer can be increased at least by one digit compared to the case of ZnS as the host material.

The second advantage is that the emitting of the area of 520 nm to 620 nm, where the existing phosphor of ZnS : Pr^{3+} shall not emit efficiently, shall be increased by MgS solid solution, and also the adjustment of emitting intensity shall become possible by depending on the amount of the MgS solid solution. Further, concerning the thin film EL element, the adjustment of the emitting intensity shall become possible also by the drive frequency. As a result, using the abovementioned second advantage, a wide range of white color display or white color illumination, which shall correspond to the suitable field from the warm white color to the daylight white color, which is the correlative color temperature of 2300 K to 5000 K can be obtained

[Example of implementation]

Herebelow, this invention shall be explained in accordance with the implementation example.

Implementation example 1

Concerning the ordinary formula of $\text{Zn}_{1-a}\text{Mg}_a\text{S} : \text{Pr}$, the characteristics of this invention is to be $a > 0$. In order to clarify that the effect of $a > 0$ is not from the impurity within the Mg raw material, especially to clarify that it is not by the oxygen impurity, which can easily mix in together with Mg, the target for the deposition and the phosphor composition is created following the flow chart of Figure 1 using the 2 kinds of the Mg material, and then the thin film EL element is created using the said target.

Both of the 2 kinds of Mg material shall be indicated as MgSO_4 and shall have at least 99.9% of the purity, however, the initial (starting) raw materials are different. Now the material, which is started from MgO , shall be indicated as (A), and the material, which is started from the high purity Mg metal shall be indicated as (B). First of all, the target which shall have the composition of $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{S} : 0.03\text{Pr}$, which is $a = 0.1$, is created in accordance with Figure 1 using (A) and (B), and it was analyzed after. As a result, it was confirmed that with the method (B), Ca became 20 ppm from 700 ppm and Cr, Mn, Fe and Cu was reduced to less than 10 ppm from 220 ppm compared to the method (A). From the result, it is assumed that the oxygen impurity density was decreased by corresponding to those impurity density.

Next, using the target of the abovementioned (A) and (B) as the deposition source, the ordinary thin film EL element of the 3-layered structure is created by the EB (electron beam) deposition technique. Y_2O_3 , which shall be commonly known, is used as the insulation layers which shall sandwich the emission layer. Example of the comparison of the characteristics of the obtained element is shown in Table 1. As it is obvious from the table, concerning the element, which shall contain the emission layers of the same layer thickness, when starting from (B) method raw material, all of the emitting starting voltage, relative luminance and frequency characteristics are better compared to the (A) method.

Table 1

Kind of the Mg raw material	Film thickness of the emission layer (μm)	Emitting starting voltage V_{th} (V)	Relative luminance L of $(V_{\text{th}} + 30)\text{V}$ (%)	Power series of frequency characteristics $n [L \propto f^n]$
A	0.66	188	100	0.71
B	0.66	162	148	0.95

Concerning the Mg containing phosphor, which is the characteristics of this invention, it shall give quite an amount of effect to each of the characteristics of the purity of the Mg raw material, in other words, the effect can be actualized only if the purified Mg raw material is used, which was discovered from this implementation example.

Implementation example 2

Concerning the ordinary formula of $\text{Zn}_{1-a}\text{Mg}_a\text{S} : \text{Pr}^{3+}$, the vapor source target, which shall have the composition of 5 levels of a value, which shall indicate the amount of MgS solid solution making the Pr^{3+} density fixed as 0.03 mol, which are $a = 0$ (comparison example), 0.01, 0.05, 0.10 and 0.15, was created. As for the use of the Mg raw material, the (B) method, which was confirmed to have good characteristics in the implementation example 1, was used.

Using the abovementioned target, the ordinary thin film EL element of the 3-layered structure was created by the same method as the implementation example 1. The thickness of the emission layer was fixed as 0.66 μm , which was same as the case of Table 1.

The relative luminance, the chromaticity coordinates and the correlative color temperature, which was calculated from the chromaticity coordinates, at the frequency of 5 KHz under the sine wave drive, were shown in Table 2. The relative luminance of the table is the relative value of the actually measured value of making $a = 0$, which shall mean that making the luminance of when the emitting starting voltage V_{th} plus 30 V of $\text{ZnS} : 0.03 \text{ Pr}$, which is the common phosphor material, which shall not have MgS solid solution, is made as the criterion.

As it is obvious from the table, when $a > 0$, the higher luminance was obtained than when the element was $a = 0$, and when $a = 0.05$, the highest value of 173% was obtained. Further, the same performance, which are phosphor composition and development of element, were tried when $a > 0.15$, however, the scattering of the luminance characteristics became large, and the average luminance was around 100%. The reason of this is assumed that because it is close to the 22 to 25 mol%, which is the limit of MgS solid solution against ZnS, which is when $a = 0.22$ to 0.25, which was conjectured from the existing examples of (1) and (3), which were mentioned in above.

Table 2

a	Relative luminance (%)	Chromaticity coordinates		Correlative color temperature (K)
		x	y	
0 (comparison example)	100	0.354	0.434	5000
0.01	104	0.387	0.426	4200
0.05	173	0.451	0.357	2400
0.10	143	0.469	0.372	2300
0.15	110	0.452	0.394	2700

Next, when paying attention at the chromaticity coordinates of Table 2, although the y value of the chromaticity coordinates is not necessarily monotony against the increase of a value, it shall have the tendency of rather decreasing, and therefore, it shows that the improvement of the luminance, which is accompanied by the increase of the

abovementioned a value, is not because of the apparent increase of y value. Further, it was discovered that the chromaticity coordinates shall also change depending on the drive frequency. For example, the chromaticity differences of $|\Delta x|$ $|\Delta y|$ at 5 KHz and 1 KHz was the maximum of 0.001 when using ZnS : Pr³⁺ of $a = 0$, however, when $a = 0.05$, the maximum was 0.021, which became larger than one digit.

Figure 2 is the emitting spectrum of when performing at the sine wave drive and 5KHz of the element, which is composed of Zn_{0.95}Mg_{0.05}S : 0.03Pr, which is $a = 0.05$, which is the value when the highest luminance was obtained. When comparing this to the emitting spectrum of ZnS : Pr³⁺, which is mentioned in the existing example (5) in above, the emitting intensity of 520 to 620 nm area was increased, and it is assumed that only by introducing 5 mol% of MgS, it shall create the mixing of J condition of Pr³⁺, which resulted to increase the emitting transition probability. When $a > 0$, beside the increase of the emitting intensity of the abovementioned wavelength area, there was a tendency that the deep red color emitting shall appear stronger than the blue green color emitting, and as a result of this, the large amount of the change in the correlative color temperature, which shall depend on the value of a , which is mentioned in Table 2, was obtained.

Figure 3 was the result of the research concerning the distribution of Mg / Zn, Pr / Zn and Y / Zn, which are the film thickness direction of the 0.8 mm² (unit is not visible) area of the 2-layer structure film by O²⁺ ion irradiation making the subject as the trial material of the 2-layer structure, which the emission layer, which shall have the composition of $a = 0.05$, was deposited for the amount of approximately 1 μm, on top of the Y₂O₃ insulation film, which was deposited on the glass substrate in advance in accordance with the creating process of the thin film EL element of the ordinary 3-layered structure. From the figure, it is seen that the distribution of the emitting ion Pr³⁺ of the film thickness direction shall correspond well with the distribution of Mg of the host material. It proves that Pr³⁺ shall introduce effectively under the existence of Mg.

Implementation example 3

The synchronization of the below mentioned compositions was performed for the purpose of the luminance comparison of when using MgS and not using MgS by excitation except by the electric field. The Pr³⁺ density of the trial material which was used for the comparison was lowered by one digit compared to the case of the implementation example 1 and 2, and the composition of the host material was made as Zn_{0.95}Mg_{0.05}S, which shall be corresponded to $a = 0.05$ and ZnS, which shall be corresponded to $a = 0$. In accordance with the flow chart of Figure 1, the abovementioned composition was measured and dry mixing (symbol 2 of the figure) was performed, then after that, 100g of the said mixture shall be filled up carefully to the transparent quartz boat, and firing was performed for 2 hours at 1000 °C at Ar discharge 200 ml / min. without performing the process of the symbol 3 of the figure. Before and after the firing, Ar gas was discharged for a whole day and night.

Next, water sedimentation applying was performed to the obtained powder phosphor material, and the powder luminance by the electron beam excitation was compared. The condition of the excitation is 27 KV of the accelerated voltage and 0.16 μA / cm² of the

density of the electric current. Based on the luminance of the $\text{ZnS} : 0.003 \text{ Pr}^{3+}$ of the common phosphor, which is equivalent to $a = 0$, in the case of the $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{S} : 0.003 \text{ Pr}^{3+}$, which is equivalent to $a = 0.05$, which is related to this invention, could obtain the luminance of 3.6 times.

[Effectiveness of the invention]

As it is explained, in this invention, by making MgS into solid solution with the host material of the $\text{ZnS} : \text{Pr}^{3+}$ of the common phosphor, the host material lattice shall be expanded in order to make the introduction of the emitting ion Pr^{3+} easy, 1.7 times of the luminance compared to the $\text{ZnS} : \text{Pr}^{3+}$ contained EL element, which is created by the same manufacturing method applying to the emission layer of the thin film EL element, is obtained. Also, by adjusting the amount of MgS solid solution, side correlative color temperature adjustment of between 5000 K and 2300 K shall become possible. The effectiveness of the MgS solid solution shall not be limited to the abovementioned thin film EL element. If it is within the field which shall have the applicable results of ZnS either past or current, even by giving the other type of energy beside electric field, the effect can be accomplished by making the best condition between the Pr^{3+} density and MgS solid solution, and the luminance of the electron beam excitation shall exceed 3 times of the luminance of the existing phosphor.

Because generally the Pr^{3+} shall generate the emitting which shall have the wide visible wavelength area, therefore, it is effective to apply for the use of the white color display element and white color illumination light, where the visual recognition is quite important, and especially it is very effective in the field, which shall require the warm white color.

Further, this invention shall create the effect by introducing Pr^{3+} to the Mg contained host material, however, even if very small quantity of the emitting ion beside Pr^{3+} is introduced, the effectiveness of the Pr^{3+} emitting shall not be damaged.

4. Simple explanation of the figures

Figure 1 is a flow chart which shall indicate the composition method of the phosphor composition which is mentioned in the implementation example of this invention and the manufacturing method of the vapor source target using the material, Figure 2 is a figure of the emitting spectrum of the thin film EL element which shall have $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{S} : 0.03 \text{ Pr}$ as the emission layer, and Figure 3 is a figure to indicate the film thickness direction structure ion distribution within the emission layer of Figure 2.

Figure 1

- 1: Sulfide treatment
 H_2S 100ml / min.
 Up to 1000 °C
- 2: Mixing the amount
- 3: Applying pressure, molding
- 4: Sintering

Ar 200 ml / min.
Up to 1000 °C
5: Deposition target
 $\text{Zn}_{1-x}\text{Mg}_x\text{S} : \text{Pr}^{3+}$

Figure 2

Vertical: Relative emitting intensity (%)
Horizontal: Wavelength (nm)

Figure 3

Vertical: Count number
Time: (min.)